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Wet-Strength Resins and Their Application

*A project of the Papermaking Additives
Committee of TAPPI's Paper and Board
Manufacture Division*

Committee Assignment No. 810506.03

Lock L. Chan, Task Group Chairman and Editor

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CHAPTER 2

ALKALINE-CURING POLYMERIC AMINE-EPICHLOROHYDRIN RESINS

Herbert H. Espy

Acronyms

The following list of chemical acronyms is used in this chapter:

- APE: "Amine polymer"-epichlorohydrin
- BHMT: Bis hexamethylenetriamine
- CMC: Carboxymethylcellulose (as its sodium salt)
- DAA: Diallylamine
- DETA: Diethylenetriamine
- EDA: Ethylenediamine
- HMDA: Hexamethylenediamine
- IBPA: Iminobis(propylamine)
- MBAPA: Methylbis(3-aminopropyl)amine
- MDAA: Methyldiallylamine
- MF: Melamine-formaldehyde
- NSSC: Neutral semichemical sulfite pulp
- PAE: Polyamide-epichlorohydrin
- PAPA: Polyalkylenepolyamine
- PAPAE: Polyalkylenepolyamine-epichlorohydrin
- PAU: Polyaminoureylene
- PDAA: Poly(diallylamine)
- PEHA: Pentaethylenehexamine
- PEI: Polyethylenimine
- PMDAA: Poly(methyldiallylamine)
- PPE: Polyamide-polyamine-epichlorohydrin
- TEPA: Tetraethylenepentamine
- TETA: Triethylenetetramine
- UF: Urea-formaldehyde

Introduction

During World War II, the need increased for durable packaging materials resistant to humidity and water. This need sparked the development of wet-strength resins. The late 1940s and early 1950s saw the development of urea-formaldehyde and melamine-formaldehyde resins of improved effectiveness. Both classes of resins required acid conditions—from alum or mineral acid—to cure effectively in paper.

Alkaline-curing amine-epichlorohydrin condensation products, related to epoxy resin adhesives, were investigated in the 1950s. The first alkaline-curing wet-strength resins to become commercially practical were polyamide-epichlorohydrin (PAE) resins, sometimes referred to briefly as “polyamide-epi” resins. These gained immediate acceptance and rapidly started to replace urea-formaldehyde resins in many applications. They offered high cost-effectiveness as well as improved absorbency in sanitary grades, reduced machine corrosion, compatibility with alkaline sizes, and other benefits. Later, polyalkylenepolyamine-epi (PAPAE) resins and “amine polymer”-epi (APE) resins were introduced commercially.

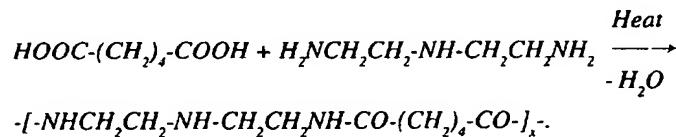
Commercially available alkaline-curing wet-strength resins are made by reacting a polyamine or an amine-containing polymer with an epoxide possessing a second functional group (typically epichlorohydrin) in water solution. The epichlorohydrin alkylates and crosslinks the polyamine to a moderate molecular weight. The crosslinking reaction is then arrested by dilution, and/or by reducing the pH to convert amine groups to their acid salts. The resins are supplied as solutions between 10% and about 35% solids.

All commercially available alkaline-curing resins are cationic and thermosetting at near-neutral and alkaline pH conditions. Thus, when added at the wet end of the paper machine, they are adsorbed onto the pulp fibers and fines. When the paper is dried under near-neutral or alkaline pH conditions, the resins resume their crosslinking to form an insoluble network that imparts wet strength.

Terminology of Polymeric Amine-epichlorohydrin Resins

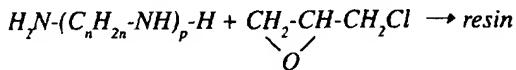
The alkaline-curing amine-epichlorohydrin resins can be categorized either by the chemistry of their backbone polymers, or by their reactive functionality. The terms “polyamide-epichlorohydrin” (PAE), “polyalkylenepolyamine-epichlorohydrin” (PAPAE), and “amine polymer-epichlorohydrin” (APE) describe the backbone polymers of the resins.

“Polyamide-epichlorohydrin” (PAE) refers, more explicitly, to poly(aminoamide)-epichlorohydrin resins. (In the European literature, these are sometimes called “polyamide-polyamine-epichlorohydrin” or “PPE” resins.) Their precursors are made by the polycondensation reaction of a polyalkylenepolyamine with a polycarboxylic acid. The most prevalent examples are those from a polyethylenepolyamine, such as diethylenetriamine (DETA), with a dibasic acid, such as adipic acid (1, 2):



With them, other condensation polymers will also be reviewed.

"Polyalkylenopolyamine-epichlorohydrin" (PAPAE) resins are made by condensing an initial polyalkylenopolyamine ("PAPA") directly with epichlorohydrin:



They also include some resins in which the polyalkylenopolyamine is linked by dihalides to form higher polyamines before the crosslinking reaction with epichlorohydrin.

As described here, "amine polymer-epichlorohydrin" (APE) resins include resins in which a monomeric amine is polymerized to an "amine polymer" precursor, which is then alkylated and crosslinked with epichlorohydrin. They include amine-substituted polymers of vinyl, allyl, acrylate, or epoxy monomers, as well as a few monoamine-epichlorohydrin resins.

PAPAE and APE resins are sometimes categorized together as polyamine-epichlorohydrin resins (3). However, the distinction between them is useful in practice, even if sometimes arbitrary chemically. On a weight basis, most PAPAE resins are less effective than the polyamide (PAE) resins, while many APE-based resins (especially of the epoxide type) are more effective.

Whether the reaction partner of epichlorohydrin is a polyamide, a polyamine, or an amine polymer, its amine groups may be primary (1°), secondary (2°), or tertiary (3°). These react with epichlorohydrin by different routes (Figure 2.1).

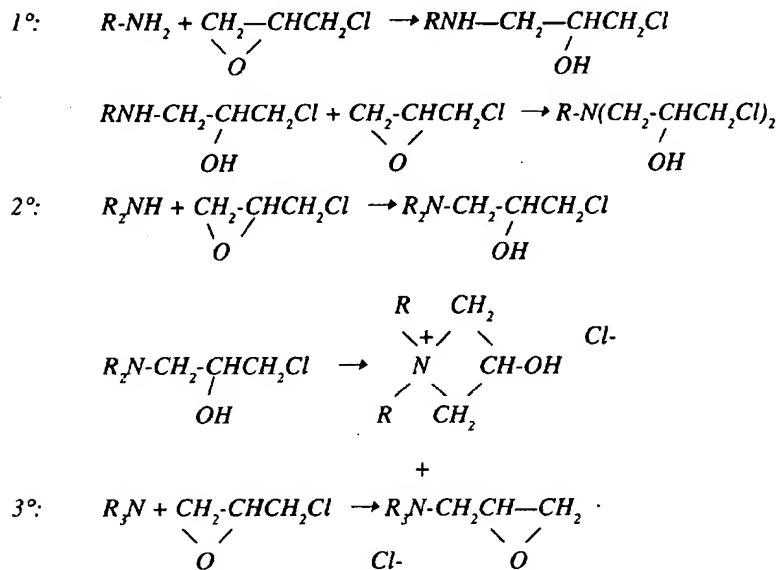


Figure 2.1. Reactions of amines with epichlorohydrin

Primary amines react with epichlorohydrin to form a chlorohydroxypropyl-substituted secondary amine, which then reacts with a second mole of epichlorohydrin as described next. Few primary amine-based polymer-epichlorohydrin products are commercially significant wet-strength resins.

Secondary amines react with epichlorohydrin to form tertiary aminochlorohydrins, which cyclize to form reactive 3-hydroxy-azetidinium salts (4-8). Since the most important PAE

resins are derived from secondary aminopolyamides, the 3-hydroxyazetidinium ring is likewise their principal reactive functional group (9, 10), and they may be referred to as "azetidinium" resins.

Tertiary amines react with epi by initial opening, then reclosure of the epoxide ring with expulsion of chloride ion, to form a glycidyl (2,3-epoxypropyl) ammonium salt. Resins based on the tertiary amine-epichlorohydrin reaction will be called "epoxide" resins. This term refers to the functionality of the resin, not to the epoxide group of the epichlorohydrin precursor of both classes of resins.*

These functional groups can occur independently of the category of backbone polymer. Thus, resins with either azetidinium and epoxide functionality have been based on backbone poly(aminoamides), depending on the kind of starting amine groups. The commercially significant azetidinium resins are principally of the PAE (polyamide) and PAPAE (polyalkylene-polyamine) type. Currently important epoxide resins are of the PAE and the APE (amine polymer) type.

The section on resin chemistry is organized according to the type of polymer backbone. However, the qualitative differences in handling, performance, and reactivity of the resins in paper depend more on the differences between azetidinium and epoxide resins than on differences among backbone polymers. Therefore, some of the discussion of applications technology is organized around the functional groups.

Classes of Polymeric Amine-epichlorohydrin Resins

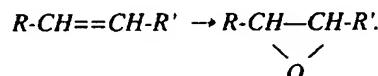
Polyamides and Other Condensation Polymers

Secondary amine-based azetidinium resins

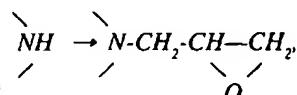
Saturated and aromatic acids

In the original patents (1, 2) for wet-strength resins of this class, the polyamides were based on saturated aliphatic dicarboxylic acids and polyalkylenepolyamines containing two primary amine groups and at least one secondary amine group. An example is the first commercial resin, derived from adipic acid and diethylenetriamine (DETA) (Figure 2.2).

*In this connection, it may be mentioned that the term "epoxidation" customarily refers to the conversion of a double bond to an epoxide.



The attachment of a glycidyl group to an amine.



is referred to more accurately as "epoxypropylation" or "glycidylation," i.e., as a specific alkylation reaction.

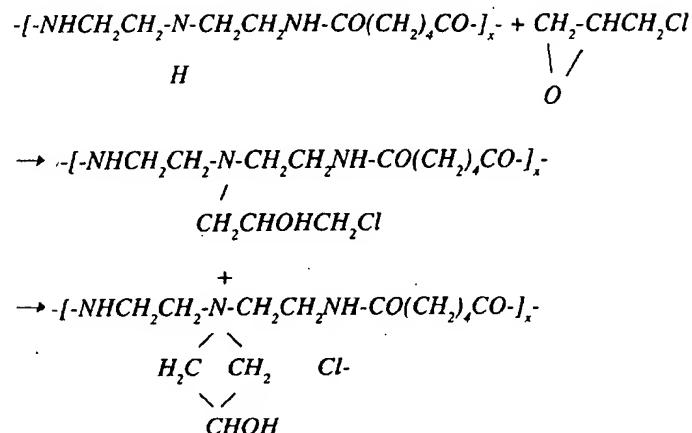
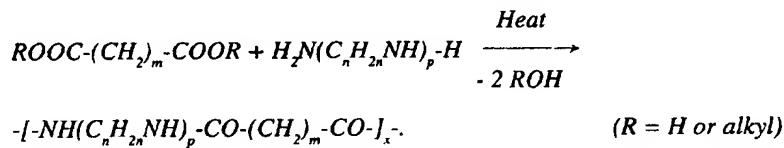


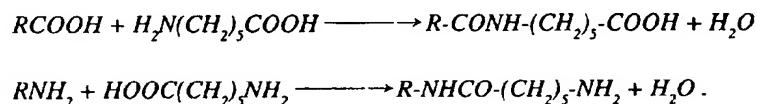
Figure 2.2. Formation of Adipic Acid-DETA Polyamide-epichlorohydrin Resins

In most known commercial PAE resins, the acid moiety (C_8 or below for reasons of solubility) is derived either from the dicarboxylic acids themselves (1, 2) or their esters (11):



The patent literature also describes analogous resins based on higher aliphatic diacids (12-15), fatty (mono)acids (16), alicyclic (17, 18), and aromatic acids (19-24), as well as aliphatic acids containing heteroatoms such as oxygen (1) or nitrogen (25-29).

Caprolactam and 6-aminocaproic acid are components of some polyamide wet-strength resins (30-39) and dewatering aids (40). They will react with either a carboxyl or an amine end group to form an amide group and regenerate a similar end group:



Copolymerization with aminocaproic acid can introduce amide-containing "spacer" units without introducing more amine sites for attaching epichlorohydrin. Aminobutyric acid and its corresponding five-membered cyclic lactam have also been described as polyamide resin components (41). Caprolactam is also used alone (42) or as the precursor of complex dibasic acids (36, 37, 43, 44) in other wet-strength resins and processing aids. Lactones (cyclic esters) have been described as coreactants with acids and polyamines in the formation of polyamide-polyester resins (45-47).

Conjugated unsaturated acids

The combination of Michael addition of amine to the double bond, and amide condensation at the ester group, has been used (48, 49) to form aminopolyamide resins based on polyalkylamines and acrylate esters (Figure 2.3).

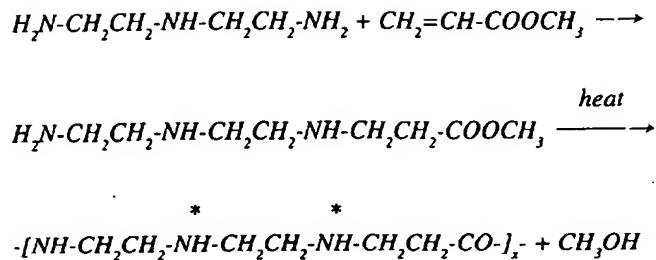


Figure 2.3. Poly(aminoamides) from acrylic esters and DETA

in which the starred nitrogens are amines that may react with epichlorohydrin. Linear (48, 49) and branched (50) resins of this type have been described.

Monoalkyl esters of maleic acid react analogously with polyalkylenepolyamines to form precursors of "poly-beta-asparagine- epichlorohydrin" wet strength resins (51, 52) (Figure 2.4).

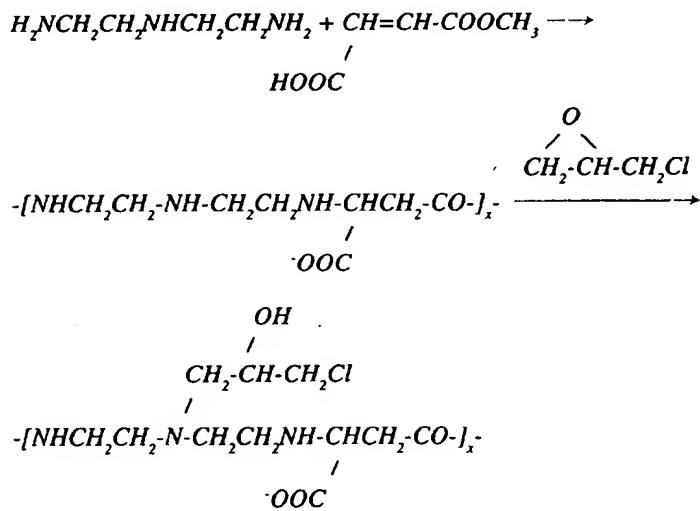


Figure 2.4. Monomethyl maleate-DETA polyamide-epichlorohydrin resins

Analogous maleic anhydride-polyamine polyamide-epichlorohydrin resins have also been disclosed (53, 54).

Resins from itaconic acid have been described (55-57) and introduced commercially. Although the double bond of the starting itaconic acid was reported to survive and to be subject to copolymerization with vinyl monomers (56), other studies (58-63) indicate that this bond actually becomes saturated by amine addition under the conditions of the polyamide condensation reaction (Figure 2.5).

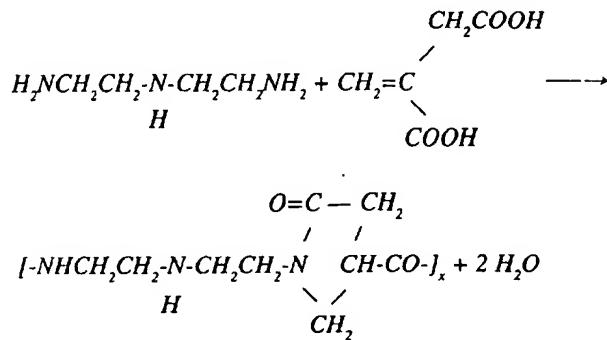
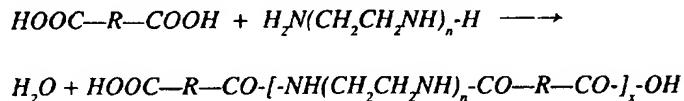


Figure 2.5. Itaconic acid-DETA polycondensation reaction

Miscellaneous condensation polymers

A polyamide resin, believed to be of commercial significance, is made by a complex four-step process (64). A polyalkylenepolyamine is reacted with excess dicarboxylic acid, e.g., oxalic acid, to form a carboxyl-terminated "base polyamide":



Reaction of the carboxyl groups with a primary-tertiary diamine “terminating polyamine” provides a “terminated base” having tertiary amine end-groups, which are then connected by a polyalkyleneglycol dihalide such as “triglycol dichloride” (1,8-dichloro-3,6-dioxaoctane) to form an “extended base” (Figure 2.6).

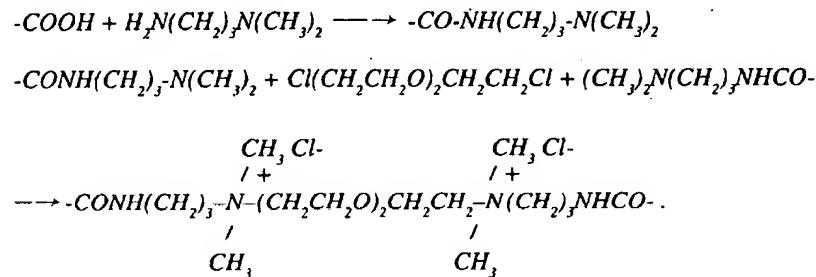


Figure 2.6. Termination and formation of “extended base”

The secondary amine groups of the original "base polyamide" segments then react with epichlorohydrin to form the wet-strength resin.

Besides dicarboxylic acids, other components of condensation polymers include urea (65-71), tolylene diisocyanate-alcohol addition products (72), dialdehydes (73), dicyandiamide (74), and guanidine (75).

Polyamine components in polyamides

Ever since the first commercial alkaline-curing wet-strength resins, the language of patent disclosures recites the list of polyethylenepolyamines from diethylenetriamine through

pentaethylenhexamine (PEHA). Mixtures of two or more polyamines are also disclosed (24, 75), as is the partial replacement of a polyamine by a diamine (1, 2). Historically, the principal polyamine component of polyamide resins has been diethylenetriamine (DETA). In the United States, at least, the PAE resins of greatest commercial importance are those based on DETA, since Food and Drug Administration clearances for their use in food packaging describe only DETA-based resins (76).

The patent literature describes the partial replacement of the polyamine component by diamines (1, 2), alkanolamines (77, 78), and polyglycols (79) to yield copolyamide or polyester-polyamide resin precursors. Mixtures of separate polyalkylenepolyamines and polyalkylenepolyamine-dibasic acid polyamides have been coreacted with epichlorohydrin (80-84). In most, the separate polyamine has been a polyethylenepolyamine, although methylbis(aminopropyl)amine has been used (84).

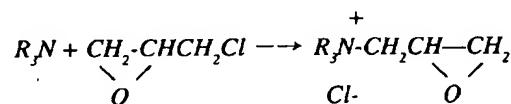
Basic nitrogen compounds such as ethylenediamine, added with resin to the pulp, have been described as curing accelerators for PAE and PAPAE resins (85).

Modified poly(aminoamide)-epichlorohydrin resins

At least experimentally, polyaminoamide precursors have been modified before the epichlorohydrin reaction (Figure 2.11), by treatment with dicyandiamide or guanidine hydrochloride (86), acrylonitrile (87), acrylamide (88, 89), ethylene oxide (90, 91), formaldehyde (92), or sodium chloroacetate (35).

Tertiary amine-based epoxide resins

In these resins, a tertiary amine reacts with the epoxide of epichlorohydrin to form a glycidyl quaternary ammonium salt:



The first condensation polymers to employ this chemistry were based on methylbis(3-aminopropyl)amine ("MBAPA," also known as methyliminobispropylamine), which was condensed by heating with urea to give a polyureylene (or thiourea to give a polythioureylene) (93), with dicarboxylic acids or esters to form polyamides (94-96) or copolyamides (97-99), or with both to give polyamide-polyureylenes (100, 101) (Figure 2.7).

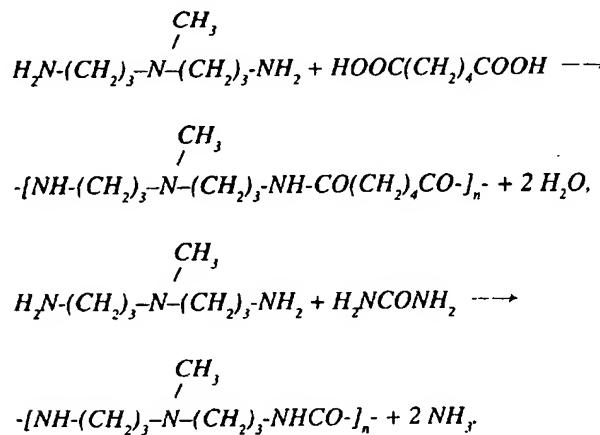


Figure 2.7. Polycondensation reactions of MBAPA

The glycidyl quaternary ammonium resins ("epoxide" resins) are characterized by high efficiency and high off-machine wet strength. As a class, they can impart more wet-strength than azetidinium resins after oven-curing, and they can develop a higher proportion of their ultimate wet-strength during the drying operation.

If left in the epoxide form as made, these resins can lose their effectiveness because the epoxide group is hydrolyzed much faster than the azetidinium group. However, their reaction with hydrochloric acid converts the epoxide groups to chlorohydrin groups (102). In the chlorohydrin form, the resins are stable in concentrated solution for a long time without loss of potential effectiveness. They are reactivated just before use, by treatment in dilute solution with enough alkali to reconvert the chlorohydrin to the epoxide form (102). The stabilization and reactivation are discussed in more detail below.

Polyamine (Polyalkylenepolyamine) Resins

A few amine-epichlorohydrin resins have been described, based on ammonia (103, 104) or methylamine or similar amines (104), alone or in combination with polyamines (105). However, polyamine-based resins have been investigated much more extensively. With a few exceptions, the polyamines are based on C₂, C₃, or C₆ alkylene units, of which the last are of the most commercial importance.

Polyethylenepolyamines (poly-C₂-polyamines)

Polyethylenepolyamine-based resins, e.g., triethylenetetramine- and tetraethylenepentamine-epichlorohydrin, were among the first to be patented (106). Other examples are based on polyethylenimine (PEI) (107, 108), or (for use in dewatering) polyethylenepolyamine still bottoms (pentamines and higher) (109). PEI crosslinked with vinylcyclohexene dioxide has also been described (110). From a study of the kinetics of the reaction of epichlorohydrin with ethylenediamine, DETA, and PEI, it has been concluded that PEI for wet-strength applications should be as linear as possible (111). Resins of this class have not become important commercially in wet-strength applications because of their modest cost effectiveness.

A number of resins have been described in which a polyalkylenepolyamine is chain-linked to a polymer before the crosslinking reaction with epichlorohydrin. These are more numerous among resins based on C₃ and higher alkyleneamines. However, polyethylenepolyamine-diglycidyl ether precondensates, such as TETA linked with the diglycidyl ether of 4,4'-isopropylidene-bisphenol, have been described as precursors of epichlorohydrin wet-strength resins (112).

1,2-Dichloroethane-linked prepolymers from tetraethylenepentamine (TEPA) or from TEPA-adipic polyamide are nonthermosetting resins that (in combination with other polymers) increase dry strength without imparting wet strength (113).

Poly(trimethylene)polyamines (poly-C₃-polyamines)

Bis(3-aminopropyl)amine (also known as iminobispropylamine or IBPA), H₂NCH₂CH₂CH₂NHCH₂CH₂CH₂NH₂, has been reacted with epichlorohydrin to make wet-strength resins, both alone (114), and as an extended prepolymer made by chain-linking with 1,2-dichloroethane (115). Poly-C₃ (and higher) polyamine-epi products have also been described as auxiliaries such as flocculants (116).

N-alkyl-1,3-propanediamines have been reacted with epichlorohydrin, directly to make paper sizing compositions (117), or with DETA-epichlorohydrin and TEPA-epichlorohydrin adducts for wet- and dry-strength compositions (118).

Poly(tetramethylene)polyamines (poly-C₄-polyamines)

Poly(tetramethylene)polyamines are not as prominent in commerce as the C₂- and C₃-based polyamines, but have been described occasionally as precursors of wet-strength resins.

Bis(tetramethylene)triamine-1,2-dichloroethane prepolymer epichlorohydrin resins have been exemplified (119). They are also included in the range of C_4 - C_{15} diamines, in a patent on the partial removal of anions from diamine-dihalide prepolymer before its reaction with epichlorohydrin (120).

Hexamethylenediamine and higher homologues (poly- C_6 -polyamines)

Hexamethylenediamine (HMDA, alternatively 1,6-hexanediamine) is made in high volume as a precursor of nylon fibers. HMDA and its higher homologues (as still bottoms from its production) have been employed as the basis of a variety of commercially significant wet-strength resins. With epi, HMDA itself has been used as its 1,2-dichloroethane prepolymer (121), alternatively with anions removed (122). Bishexamethylenetriamine (BHMT, alternatively dihexamethylenetriamine) has also been used in epichlorohydrin resins (121).

Miscellaneous

Non-thermosetting resins, e.g., from methylamine, ethylenediamine (EDA), and epi, or TEPA-adipic polyamide-epi, TEPA-dichloroethane, TEPA-adipic polyamide-dichloroethane, have been used in conjunction with other polymers as dry-strength resins. Their ionic bonds strengthen dry paper, but split when paper is wet (113).

Sulfur-containing precursors from the reaction of polyalkylenepolyamines with SCl_2 , $SOCl_2$, SO_2Cl_2 , etc., can react with epichlorohydrin to yield retention aid and adhesive resins (123, 124). In more-distantly related chemistry, epichlorohydrin-bisphenol A resin and DETA can form an epoxyamine, which is reacted in turn with a carboxyl-terminated polyester, for wet strength (125).

“Amine Polymer” Resins

Poly(diallylamine) resins (azetidinium-type)

The radical-initiated polymerization of diallylamine (DAA) acid salts yields poly(diallylamine) (PDAA). The secondary amine groups of this prepolymer can react with epichlorohydrin analogously to those in poly(aminoamides) (122, 126, 127) (Figure 2.8). Process modifications have been described, in which halide ions have been removed from the prepolymer before the epichlorohydrin reaction (122). Resins based on DAA copolymers (128) or terpolymers (129) are known.

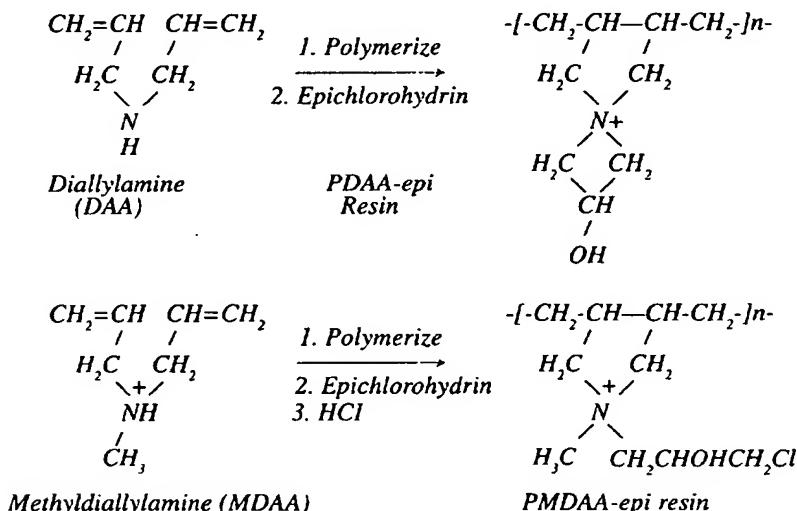


Figure 2.8. Formation of PDAA- and PMDAA-epichlorohydrin resins

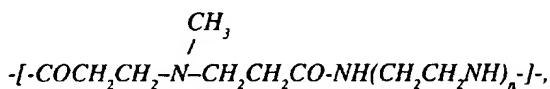
Poly(alkyldiallylamine) resins (epoxide-type)

The analogous polymerization of alkylidiallylamines such as methylidiallylamine (MDAA) yields tertiary amino polymers. These can react with epichlorohydrin to form glycidyl quaternary ammonium polymers, that can be stabilized as their chlorohydrin forms (126-128, 130-133) (Figure 2.8). Resins from copolymers of DAA (128) or MDAA (126, 129) have also been described.

Poly(MDAA)-epichlorohydrin resins (after alkali reactivation) are probably the most effective known alkaline-curing wet-strength resins on a weight basis. However, their machine broke is harder to repulp than that of most other resins (see below).

Miscellaneous

A primary amine can be treated with two moles of acrylamide to form a tertiary amino-bisamide. Reaction of this with a polyalkylenepolyamine forms a polymer.



which can react with epichlorohydrin (presumably at both secondary and tertiary amine groups) to form a wet-strength resin (134).

Various tertiary amino-alkyl substituted polyacrylates (135-139) or polyethers (140, 141) have been treated with epichlorohydrin, then HCl, to form base-activatable wet-strength resins. Also, some polyacrylics have been treated with polyalkylenepolyamines to form (poly)aminoalkylamide side chains, which have then been reacted with epichlorohydrin (142-144).

Epichlorohydrin derivatives of other primary amine-substituted polymers include those of poly(vinylbenzylamine) (145, 146), and poly(allylamine) (147). Ammonia-epichlorohydrin-thiourea resins have also been described (148). None of these miscellaneous resins are believed to be important commercially in North America.

Crosslinking Agents

Although other epihalohydrins are disclosed in the patent literature (1, 2), epichlorohydrin is the crosslinking component used in alkaline-curing in wet-strength resins of known commercial significance. Its HCl adduct, 1,3-dichloro-2-propanol, has been described as an alternative (84, 106, 143, 149-152). Dichloropropanol would form the same initial functional group as epichlorohydrin after pH adjustment of the product (Figure 2.9).

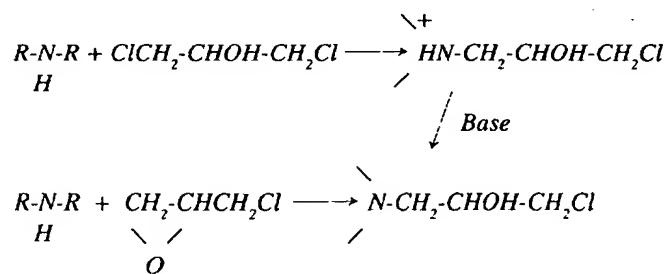
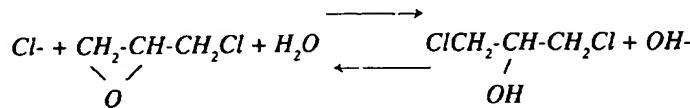


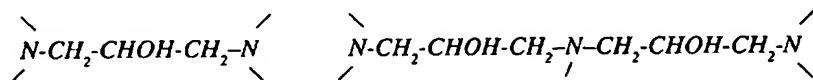
Figure 2.9. Equivalent reactions of epichlorohydrin and dichloropropanol with amine

Epichlorohydrin and 1,3-dichloro-2-propanol are interconvertible in solution, the position of the equilibrium reaction depending on the pH and chloride ion content of the solution:



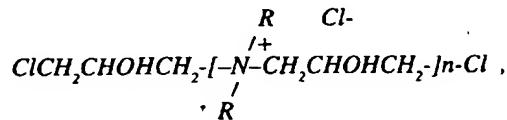
An alternative to the use of epichlorohydrin is the generation of chlorohydroxypropyl groups in situ, by quaternizing a tertiary amine polymer with allyl chloride, then generating the chlorohydrin by adding HOCl to the allylic double bond (153).

Epichlorohydrin-ammonia condensation products have been described, in which at least some of the $\text{C}_3\text{-}$ crosslinks of PAE resins are supplanted by $\text{C}_3\text{-N-C}_3$ linkages:



The polyamide from a polyalkylenepolyamine and a dibasic acid (ester) may react concurrently with ammonia and epichlorohydrin (154), with a preformed ammonia-epichlorohydrin precondensation product (154), or concurrently with epichlorohydrin and a preformed ammonia-epichlorohydrin product (155).

Products of the precondensation of secondary amines with epichlorohydrin,



have been used to crosslink poly(aminoamides). The resulting resins have been described as (dry) strength resins (156), but are used principally as retention and drainage aids (157-159).

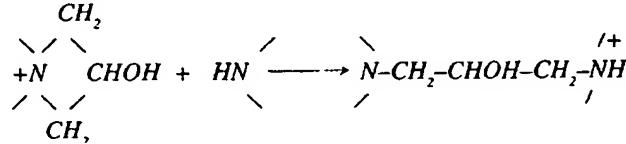
The use of glycidyl sulfonate esters or 2-hydroxypropane-1,3-bis-sulfonates with mono- or polyamines, including poly(aminoamides), has been disclosed as a way to reduce the organochloride content of mill effluents (160). 1-Acyloxy-2-hydroxypropyl compounds, resulting from the reaction of halohydrins with ammonia or amines and inorganic base, then with halogen-free acids, are also claimed to give wet-strength resins with reduced chloride content (161). A similar reaction sequence using sulfonic acids has also been described (162).

Vinylcyclohexene dioxide has also been described as a crosslinker with polyethylenimine in wet-strength resins (110).

Resin Stabilization

Azetidinium resins

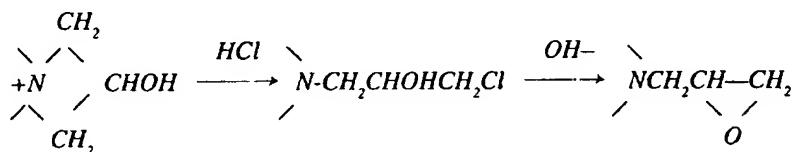
In PAE resins based on polyalkylenepolyamines, a principal crosslinking reaction is probably that of amine groups with 3-hydroxyazetidinium rings to form a $\text{C}_3\text{-}$ crosslink:



After a resin has reached the desired viscosity, indicating an effective molecular weight, the crosslinking reaction must be arrested to avoid gelation in storage. The resin is customarily

stabilized by dilution and/or acidification to inhibit further crosslinking. The acid salts of the remaining amine groups are less reactive toward the azetidinium rings than were the free amines at higher pH. In principle, any acid strong enough to protonate the amine groups of the resin will serve. Combinations of weak and strong acids, such as formic and sulfuric, have been claimed to improve stability of PAE wet-strength resins by buffering them against pH drift (163, 164). When the resin is added to a pulp slurry, the normal alkalinity of the water is sometimes enough to raise the pH to where the resin, once sorbed on pulp, can crosslink and become insoluble as the paper is dried.

Reportedly, hydrochloric acid can be used under more strenuous conditions to open the hydroxyazetidinium groups to tertiary aminochlorohydrins. The resins can be reactivated with alkali just before use, to convert the aminochlorohydrins to the more reactive amino-epoxides (165).



Polyamine-epichlorohydrin reaction products stabilized with halogen-free sulfonic acids have been claimed to produce resins containing sulfonate ester groups, with reduced chloride content (162, 166). Salts, e.g., those of Mg, Ca, Zn, and Al, reportedly stabilize PAE resin solutions by coordination with the polymer (167). PAE resins have also been stabilized by postaddition of either formaldehyde (168) or dimethyl sulfate (169).

Epoxide resins stabilized as chlorohydrins

Quaternary ammonium epoxide resins, derived from condensation polymers and amine polymers containing tertiary amine groups, are more reactive than the 3-hydroxyazetidinium resins derived from secondary amine polymers. If left in concentrated solution, they rapidly gel; if diluted, the epoxide groups are inactivated within hours to a few days by hydrolysis to inert glycol groups.

However, as mentioned above, they can be converted to chlorohydrins by reaction with hydrochloric acid (102) (Figure 2.10).

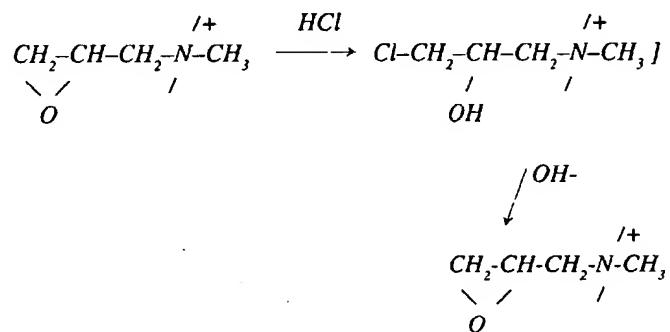


Figure 2.10. Stabilization and reactivation of epoxide (glycidyl ammonium) resins

This process of stabilization may be distinguished from the usual pH adjustment of the azetidinium resins, which simply involves conversion of amine groups to their acid salts. Rather, it also converts essentially all of the thermosetting groups of the resin to a less reactive form. Thus, more acid is required than that needed merely to adjust the pH.

The chlorohydroxypropyl groups of the stabilized resin can be reconverted to epoxide groups by brief reaction (a few minutes in the cold) with alkali. The rate of reaction increases with increasing pH. Like the stabilization, the reactivation is more than a simple "pH adjustment" to pH 11 or above. For maximum resin efficiency, a stoichiometric amount of alkali is needed to convert all of the chlorhydrin groups to epoxide. However, an excess can accelerate hydrolysis of the epoxide groups. Manufacturers' instructions should be followed. The reactivation is usually done in dilute solution to avoid premature gelation, and good stirring is essential to avoid locally excessive concentrations and consequent gel formation.

Mechanism of Wet-strength Resin Development

Adsorption of Resins on Pulp

Pulp saturation and electrokinetic behavior

For a wet-end additive to impart wet strength, it must be adsorbed on pulp from aqueous medium and be retained, and (with the possible exception of polyethylenimine) it must form an insoluble crosslinked network.

Alkaline-curing resins are cationic because of the quaternary ammonium nitrogen of their azetidinium or glycidyl-ammonium groups, augmented by some protonated tertiary amine groups. Pulp fibers and fines in water dispersion have a negative surface charge. This negative charge arises from the formation of an electrical double layer when a solid surface is immersed in water, and also arises from the presence of carboxyl (and sometimes sulfonate) groups in the pulp (170). It seems generally accepted that the initial attraction of resin to pulp is primarily electrostatic. The cationic macromolecules are attracted to the negatively charged surface of pulp fibers and fines. Once the resin is attracted to the pulp, its retention (before curing) appears to be due to ion exchange with the counterions of the carboxyl groups, as shown by studies with PAE resins (170-172). The amount of PAE resin retained under standardized handsheet conditions increases with the carboxyl content of the pulp (173), and also with pH (174). The carboxylate groups also react with the resin on curing to contribute to wet-strength development (see below). Typically, unbleached kraft has the highest content of pulp carboxyl, followed by hardwood kraft, softwood kraft, and finally bleached sulfite. Pulps with high alpha-cellulose content and low carboxyl (because of low hemicellulose content) are correspondingly less responsive to wet-strength resins.

Thus, the resins are substantive to pulp; they are spontaneously adsorbed from aqueous solution onto fibers and fines. The first added resin is completely adsorbed. As increasing amounts of resin are added, the wet strength usually continues to increase but more slowly, showing diminishing returns. In part, this happens because the negative sites on the pulp approach saturation, so that further increases in resin furnish do not cause proportional increases in the resin retained. However, even on a retained-resin basis, the initial increments of resin are the most effective in developing wet strength.

Pulp variables

Both pulp consistency and contact time affect resin retention. Davison (175, 176) has shown that although most of the eventual total amount of resin is rapidly adsorbed within the first few seconds after resin addition, some continues to be adsorbed over several minutes. At equal exposure times, the process is more rapid and complete in thick stock than in thin. Thus, it is usually advisable to add resin to thick stock well back in the system. In some systems, resin may be added before mild refining without adversely affecting efficiency. Sometimes, resin can be used more efficiently by adding it to long-fibered stock, before blending with other pulps such as hardwood or secondary fiber.

When possible, the resin should be diluted before it is added to the stock system. Since resin adsorption is rapid, diluting the resin will promote its more uniform distribution over all the fibers and fines. A dilution ratio of at least 10:1 is recommended. Fresh water is preferred, because white water or other kinds of dilution water may contain anionic contaminants which can complex with the cationic resins to reduce their efficiency. Good agitation is also important for uniform distribution of the resin.

The degree of previous pulp refining can affect the performance of polyamide resins. At the higher furnishes of resin, a more highly refined stock (i.e., lower freeness) will develop more wet strength because the higher surface area of the fines, in particular, allows it to retain more resin (171, 177). At lower resin furnish, the effects of stock freeness are less pronounced because even the less beaten stock has enough surface area to retain most of the resin, so that creating more surface area by refining gives no further advantage. Resin of high molecular weight is retained better than that of low molecular weight (171).

Resin-cellulose Crosslinking Interactions

General mechanisms

Once the resin is retained on the pulp, it may develop wet strength in the dried sheet by several mechanisms. Different authors count and name the mechanisms differently. The definitions often overlap conceptually, and at least some resins may function by more than one of these mechanisms. For the present discussion, they can be classified as:

1. "Preservation," "restraint," or "homo-crosslinking" (178):

The crosslinking of the resin with itself, without forming covalent bonds to cellulose or hemicellulose, either:

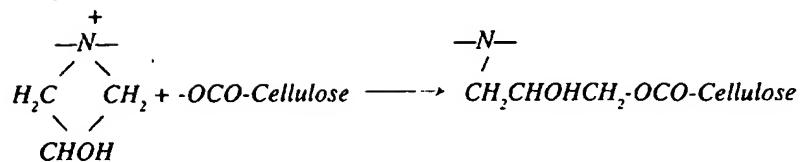
- (a) within the hemicellulose, i.e., an interpenetrating network, or
- (b) surrounding the area (volume) of fiber-fiber contact, impeding swelling and holding the fibers within hydrogen-bonding distance.

2. "New-bond," "reinforcement," or "cocrosslinking" (178): direct covalent linking of cellulose to cellulose, through a resin molecule or network of resin molecules.

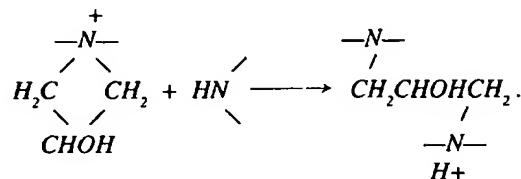
In a classic study, Kennedy (179) compared the restraining action of melamine-formaldehyde resin in hemicellulose to a hair-net around a balloon, restraining its swelling. This model implied an external restraint to the degree of fiber swelling by water [mechanism 1(b)], although the context of the discussion did not rule out either the interpenetrating-network model or the direct linking of cellulose. To pursue this analogy, then, the "reinforcement" mechanism of direct crosslinking would then be comparable to lightly vulcanizing the "balloon."

Azetidinium resins

Model compound studies, using sucrose (180) or methyl glucoside (10) suggested that PAE resin does not react with the hydroxyl groups of cellulose, and that it imparts wet strength not by new bonding but by reducing the access of water and its swelling of the pulp (presumably by self-crosslinking). However, Cheradame and Viallet (181) have seen PAE (and urea-formaldehyde) resins as forming chemically crosslinked fiber bonds. A study (182) of the insolubilization of cellulose by alkaline-curing resins also showed little or no reaction of azetidinium-type resins with cellulose hydroxyls. However, observations of the wet-strength response of pulp to PAE resin below and above the amounts corresponding to pulp carboxyl, and of the strength from PAE resin-carboxymethylcellulose (CMC) combinations, suggest that PAE resin can react with the carboxylate ions of hemicellulose, even though it may not react with the hydroxyl groups:



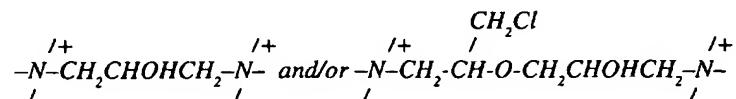
Once the carboxyl groups have reacted, additional resin tends to react by self-crosslinking:



Per unit resin retained, the reaction of PAE with carboxylate appears to produce more wet strength than does its self-crosslinking to form $\text{N-CH}_2\text{CHOHCH}_2\text{-N}$ links.

Epoxide resins

Unlike PAE or poly(diallylamine) resins, a glycidyl quaternary ammonium resin (102, 165) was able to insolubilize bleached kraft paper toward cupriethylenediamine, a solvent for cellulose. This indicates that at least some of the resin crosslinks the cellulose (182). Since the amine solvent can cleave the ester bonds (that would be formed between epoxide groups and pulp carboxylate), the resin is believed to react with hydroxyls as well as with carboxylate. However, self-crosslinking of the resin can occur concurrently, probably involving amine-amine crosslinking either directly or through intermediate ether links:



Papermaking Variables

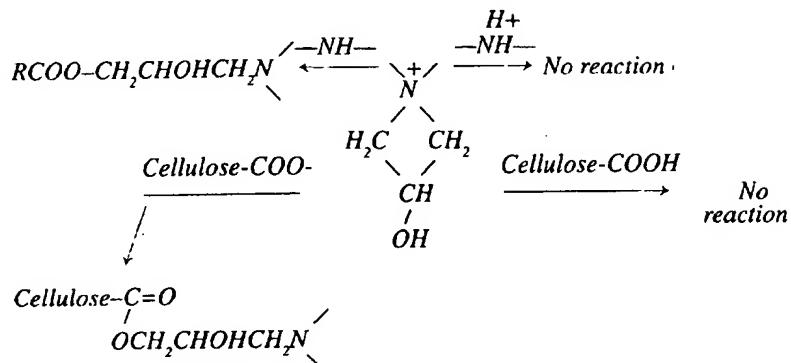
Wet-end Conditions

Electrophoretic mobility studies

Electrophoretic mobility (EM) titrations of PAE resin on pulp and fillers have been investigated extensively, e.g., the effects of metal cations present (172, 183, 184), and the relation of EM to the retention of fines and fillers (183-186) and to pulp dewatering and filtration parameters (177, 187-191).

pH

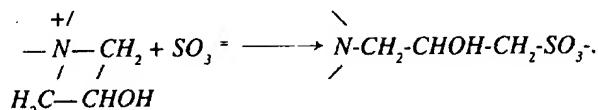
A wealth of paper mill and laboratory experience is symbolized by a few publications (173, 176), showing that PAE and other alkaline-curing wet-strength resins are most often used in a pH range of 6 to 8, but their efficiency is quite adequate in the pH range 5 to 9. As the pH is lowered to 5 and below, the efficiency of the resin can drop slightly, for two reasons. If the pH goes too low, the self-crosslinking of the resin will be impeded because the free amine groups will be converted to their protonated (ammonium salt) forms, which will not react readily with azetidinium groups. Also, the anionic carboxylate (RCOO^-) groups on the pulp will be converted to the electrically neutral carboxyl (RCOOH) groups, reducing the number of anionic sites that retain and react with cationic resin (Figure 2.11).



Mineral content: salts, hardness, alum

Modest levels of hardness can improve resin performance; polyamide resins can become more efficient as calcium hardness increases up to around 100 ppm. However, high levels of hardness can adversely affect the wet-strength response of polyamide resins. The interference is primarily with resin retention; observations of electrophoretic mobility of pulps indicate that calcium complexes with some of the carboxylate groups that would otherwise attract polyamide resin (172). Calcium ions also reduce pulp swelling (192).

Bicarbonate and carbonate ions have a specific catalytic effect on wet-strength development by azetidinium-type PAE resins (193) and epoxide resins (194), causing higher wet and dry strength from a given resin dosage under given drying conditions. The effect is not due to pH, since papermaking systems using other bases at the same pH do not show the effect. At low dosages of PAE resin, high concentrations of sulfate ions can reduce wet-strength response. This may result from shrinking of the hydrodynamic volume of the adsorbed polymer, so that isolated macromolecules are less able to reach each other to crosslink. At high dosages of resin, high concentrations of sulfate (several hundreds of ppm, or 1–10 millimolar) can improve resin performance, probably because any shrinkage of hydrodynamic volume is more than compensated by increased resin adsorption. Although sulfite ion is of the same charge type as sulfate, at high concentrations it can start to degrade resin performance, because it can convert some azetidinium rings to nonreactive sulfonate salts:



Temperature, residence time

Up to a point, increasing residence time improves the retention and wet-strength response of alkaline-curing resins on pulp. However, in hot stock with long exposure times, polyamide resins (as well as acid-curing urea-formaldehyde resins) tend to lose efficiency (195). In the polyamide resins, the polymer backbone is relatively stable, but some of the reactive azetidinium groups may be hydrolyzed. Another reason for lower effectiveness is polymer migration away from the surface and into the pores of the fiber (10, 172, 196; 197).

Anionic contaminants

Anionic contaminants in the water, such as the residues from kraft or neutral semichemical sulfite (NSSC) pulping, can interfere with the sorption of polyamide resins on pulp. Cationic and anionic polymers can form precipitates or complexes of variable composition, depending on the ratio in the starting mixture. Small amounts of cationic resin, added to a stock contain-

ing large amounts of ligninsulfonate, can form a complex with an overall net negative charge, which is of limited attraction to the anionic pulp. The loss of wet-strength efficiency can be considerable. Thorough pulp washing, if possible, can remove the contaminants and greatly improve the performance of the resin.

Interactions with dyes

Cationic resins such as PAE, PAPAE, and APE resins can alter the intensity of paper dyes by acting as retention aids. They may alter the tint of the dyes as well, but the effect of a particular resin on a particular dye must be determined individually.

Conversely, many anionic dyes will interfere with the effectiveness of PAE and other alkaline-curing wet-strength resins. This is especially true in deep shades, where the high anionic dye furnish may react with the cationic resin to form a complex with a net anionic charge, poorly retained on the pulp. Chemically similar dyes can have quite different effects on wet-strength efficiency. Therefore, unfamiliar dyes should be tested before introducing them to the machine. High levels of the following dyes in particular are potential interferers: Direct Yellow 11, Direct Orange 15, Direct Red 23, Direct Blue(s) 15, 86, and 218 (176).

If dye interferences occur, the adverse effects can be at least partly offset by using carboxymethylcellulose (CMC) in conjunction with the polyamide resin at a CMC/resin solids ratio of about 1:3, and to add the dye to the system last (176). (The resin will then be complexed preferentially with the CMC which improves wet strength; dye added later would interfere less with the resin than if it were present at the beginning.) Also recommended are the use of a dye fixative, and increasing the alkalinity of the system, specifically with sodium bicarbonate (176).

Optical brighteners, being specialized anionic dyes, can interact like visible dyes with cationic resins (198). Industrial experience has shown that some polymeric amine-epichlorohydrin resins can quench the fluorescence of optical brighteners; reciprocally, excesses of the anionic brighteners can interfere with retention of the resins. As with conventional dyes, the interaction of a specific brightener with a specific resin should be determined case-by-case.

Chlorine

Polyamide wet-strength resins can function well and show near-optimum efficiency over a wide range of water chemistries, but there is one water component that should be particularly avoided: positive chlorine or "active chlorine," such as bleach plant residuals and the like. Active chlorine compounds such as chlorine and hypochlorite are used in broke reworking, to break down the polymeric resin network. Bleaching or repulping residuals can break down freshly added wet-strength resin as well. In such cases, the stock should be treated with an antichlor (reducing agent) such as sodium sulfite, before adding the resin. Because sulfite can attack the functional groups of PAE and other polymeric amine-epichlorohydrin resins, a large excess of antichlor (more than 10–20 ppm in the white water) should be avoided.

Color bodies

In some systems, color bodies may be present as natural components of the water supply, or as pulping residuals. Polyamide wet-strength resins can also function as retention aids. If the resin retains the color bodies in the sheet, they can affect sheet brightness. Brightness comparisons of handsheets made in deionized water (salts removed, organics still present) and distilled water (both removed), showed that PAE resins have little direct effect on brightness, but can indirectly affect it by retaining color bodies (195).

Dry-end Conditions

Drying

Because alkaline-curing resins are thermosetting, the drying conditions are all-important for determining the level of wet strength in the paper coming off the machine. For the paper-

maker, the consequence can be that the same resin may perform differently in the same grade of paper dried to the same moisture specification, but made on different machines—if the machines dry at different rates, with different profiles of temperature and sheet moisture versus drying time. The difference in these profiles can also show up as differences in resin performance between wet-crepe and dry-crepe production, or between different basis weights, as well as in the relative performance of two resins (176).

Aging/artificial curing

In accelerated aging, the strength response of polyamide resins depends on both time and temperature. Higher temperatures produce the maximum wet tensile response more quickly. However, wet-strength can continue to increase even after strenuous curing, e.g., 140°C for two hours (174). Excessive artificial curing may develop more wet strength than would be actually attainable on natural aging. In typical bleached kraft pulps, PAE resins cured at 80°C for 15–30 minutes will normally reach wet strengths equivalent to those after several weeks of aging under normal storage (176).

The choice of an artificial oven-curing cycle is a matter of trade-offs. In actual mill operations, a 30-minute curing time may be excessive because mill operators will not learn the actual level of wet strength until much additional paper has been produced. If this is unacceptable, a shorter time at a higher temperature is often established. In some tissue and toweling operations, a curing cycle of 4–5 minutes at 105°C is typical. The problem with a short hot cycle is that the time for the oven temperature to recover after opening may exceed the whole cycle time. That, and undocumented differences in operators' technique, can contribute to variability in the measurement. Specific curing techniques for a given mill application should be studied carefully. The manufacturer should determine the relationship between natural aging and time/temperature curing of a sheet for each combination of resin and paper grade. Sometimes, the relative performance of two resins can be considerably different in naturally aged sheets than in artificially cured sheets.

The strength measurement used for quality control should be considered carefully. Many mills routinely use the percentage wet/dry strength as a quality control criterion. For regular production, this is a good criterion because it dissociates any changes in performance of the wet-strength resin from the normal random fluctuations in the dry strength on which that wet strength rides. However, it may be a deceptive criterion in trials, when two different classes of wet-strength resins, different refining conditions, etc., are compared. One resin may give not only more wet strength than another, but an even bigger increment of dry strength. Thus, one resin might give higher absolute values of both wet and dry strength, yet show about the same percentage wet/dry as the other. Both absolute and percentage values testify in different but complementary ways, about how successfully the handling and use of a resin has matched its chemistry.

Broke repulping

In cured PAE resins, the amide groups in the polymer backbone are not easily hydrolyzed, and in PAE and PAPAE resins the amine nitrogen-carbon bonds of the crosslinks between chains are not hydrolyzable. Therefore, the wet strength imparted by azetidinium-type resins is permanent rather than fugitive, and proper attention to special techniques is required for successful broke reworking. Especially in bleached systems, a combination of mechanical energy and an oxidizing agent can be highly effective—especially in bleached papers.

The mechanical equipment should be a high-attrition pulper with a high-speed rotor, working at high consistency (over 3%). Such a pulper can do most of the work of repulping. A deflaker, which can provide violent action without appreciably affecting freeness, can de-speck undefibered pulp and complete repulping.

Chlorine, as such (199) or as hypochlorous acid (HOCl) or hypochlorite salts (200-202), can effectively repulp PAE (201, 202) and PAPAE resins (199, 200). For example, to defiber bleached wet-strength towel usually requires approximately 0.5-2% hypochlorite ion (based on pulp), at pH 6.5-7. In this pH range, the hypochlorite is present predominantly as hypochlorous acid. At higher pH, the predominant species is hypochlorite anion which reacts less rapidly. At lower pH, chlorine may be formed and evaporate unreacted from the system. Temperatures should be about 50-55°C; higher temperatures slow the repulping by hypochlorous acid (201).

Despite earlier speculation (201), HOCl probably does not irreversibly attack the amide groups of PAE resins. There is no chemical precedent for the hypothesized conversion of -CONH- groups to -C(Cl)₂-NH- groups by aqueous hypochlorous acid. The degradation of both PAE (201) and PAPAE (200) resins, the latter lacking amide groups, suggests an attack at the tertiary amine loci of crosslinks. A CH₂-N bond of either the backbone or a crosslink is probably cleaved to a secondary amine and an aldehyde (203). PAE resins crosslinked with ammonia-epichlorohydrin reaction products are reported to be repulped more readily than conventional PAE resins (155, 204).

Although hypochlorous acid and sodium dithionite (Na₂S₂O₄, also known as sodium hydrosulfite) are both used as bleaches, they act by different mechanisms. HOCl is an oxidizing agent; Na₂S₂O₄ is a reducing agent. Dithionite has little or no effect as a repulping agent for PAE resins, consistent with its lack of reactivity toward amines (such as the crosslink sites on wet-strength resins).

In unbleached systems, hypochlorite may be consumed in side reactions that bleach the pulp rather than degrade the resin network. Besides the proper mechanical defibering equipment, elevated pH (11-12, using NaOH) and temperature (ca. 70°C) are recommended (201). Overheating the broke in an effort to defiber it can sometimes cause additional resin curing, and can thus be counterproductive.

Recent concern about potential generation of organic chlorides in effluents has awakened interest in chlorine-free oxidizing agents. Persulfate (S₂O₈⁼) salts such as ammonium, sodium, and potassium persulfate under hot alkaline conditions (70°C or above, pH 10) can effectively repulp wet-strength broke containing PAE or PAPAE resins (205).

The preferred repulping techniques for repulping epoxide-type resins depend on the resin backbone. Resins based on condensation polymers such as tertiary amino polyamides can be repulped fairly readily by strong alkali alone. Hypochlorite also degrades these resins almost as readily as azetidinium-type PAE resins, at pH 9 and above. However, some other classes of epoxide resins may be more difficult to repulp, even with high dosages of hypochlorite, and depend more strongly on mechanical attrition.

Analytical Methods

Qualitative

Since melamine-formaldehyde (MF) and urea-formaldehyde (UF) resins are degraded by acid, and alkaline-curing resins require neutral hypochlorite or alkali, secondary fiber recovery from recovered paper requires methods of identifying the wet-strength resin present in paper.

Qualitative and quantitative test methods for identifying MF, UF, PAE, and PEI resins in paper have been reviewed (206-209), along with methods of treating the identified broke (207). PAE resins can be hydrolyzed to their parent straight-chain dibasic acids, esterified, and characterized by gas chromatography (210). However, methods to distinguish PAE or PAPAE resins both uniquely and simply are few. Extract pH can provide a clue, since these resins are usually used under neutral to alkaline conditions, and MF and UF resins require acid conditions. An extract pH near 6 or higher usually indicates a PAE or PAPAE resin. A pH of 5 or lower suggests a formaldehyde-based resin, but is less certain because some manufac-

turers use PAE resins below the optimum pH range. The distinction can also be obscured because the extract pHs can be closer to each other than the original stock pHs.

The rate of disappearance of wet strength in the presence of hypochlorite can also help distinguish the alkaline-curing PAE and PAPAE resins from acid-curing resins. On treatment with hypochlorite solution, paper made with PAE resin loses wet strength in 1-2 minutes. UF resins require substantially longer times (211).

The identification of PAE or PAPAE resins in machine deposits cannot be described by a simple qualitative analysis scheme, even when a complete list of intentional additives is available. Components of a deposit are often tentatively identified by comparison of the infrared spectra of the deposit and known additives to the paper furnish. PAE and PAPAE resins have similar patterns of absorption in the region between 900 and 1250 cm^{-1} ; PAE resins also have strong absorption bands due to the amide carbonyl group between 1500 and 1650 cm^{-1} . Infrared spectra should be compared with caution, because other components such as retention aids, dye fixatives, flocculants, etc., or their combinations, can exhibit absorption bands like those of PAE resins.

Quantitative

According to a published method, PAE resins in mill effluents may be determined by sorption on silica gel and dyeing with a copper-eosin complex (212). A relative accuracy of 10-15% is claimed, for concentrations in the range of 5-40 micrograms per liter. Methods of analyzing the resins in white water by using a dye have also been described (208).

Nitrogen analysis is the most straightforward method of analyzing for alkaline-curing wet-strength resins in paper. It is necessary to know the nitrogen content of the resin itself to convert percent nitrogen to percent resin. Results will be more accurate if the nitrogen content of a pulp blank is also determined. This method is valid only if the wet-strength resin is the only nitrogen-containing species in the system. If nitrogenous synthetic fibers, retention aids, dry-strength resins, etc., are present, nitrogen analysis will not distinguish among them.

It is possible to stain wet-strength papers with an anionic dye that will be retained in proportion to the amount of cationic resin in the sheet. A sheet containing PAE resin can be stained with excess dye (e.g., Acid Red 26, C.I. 16150) in acid solution, rinsed to remove excess dye, and dried. The resin content can be determined either by brightness measurements, or by extracting the retained dye with alkali and measuring the extracts colorimetrically. The method requires calibration against sheets of known resin content, as determined by nitrogen analysis (213).

A method of determining PAE and PAPAE resins in paper or water has been outlined (214), that involves digestion of the resins to ammonia and nitrogen compounds. These are determined as $\text{HgI}_2 \cdot \text{HgNH}_2\text{I}$ with Nessler's reagent, or as NH_2OH with ferric ion (214).

Combinations With Other Polymers

Other Cationic and Neutral Polymers

Alkaline-curing resins have been used not only alone, but in combination with other polymeric materials for wet and dry strength. PAE resins have been used in combination with starch (215, 216), N-chlorocarbamoylethylated starch (216), dialdehyde starch (217, 218), polyacrylamide-glyoxal resin (219), anionic polyacrylamide (220) and glyoxal-modified acrylamide-acrylic acid copolymer (221), hydroxyethyl cellulose (222, 223), and anionic latex (224). Among PAPAE resins, combinations of tetraethylene-pentamine (TEPA)-epichlorohydrin resin with starch (225) or guar gum (226) have been claimed to improve paper strength.

Anionic Polymers

It was noted above that large amounts of anionic polymeric materials such as ligninsulfonate and other pulping residues, can interfere with the retention of cationic alkaline curing resins,

especially in semichemical and unbleached sulfite pulps. In clean systems, however, intentionally added anionic polymers can interact synergistically with PAE, PAPAE, and APE resins to improve paper strength properties. Beneficial effects require the use of controlled ratios of anionic to cationic polymer, such that retention of the latter is improved rather than inhibited.

Nonthermosetting cationic polyamine-epichlorohydrin polymers have been used in combination with anionic polymers such as anionic polyacrylamide (227) for dry strength without wet strength. Sometimes these have been used as preblends stabilized electrolytically by salts (228-230), e.g., a nonthermosetting TEPA-adipic polyamide-epichlorohydrin resin-anionic polymer mixture for dry strength.

Wet-strength grades of PAE resins can exhibit synergistic improvements in both wet- and dry-strength response when used in combination with carboxymethylcellulose (CMC) (231-233), cationic starches (231), acrylamide-acrylic acid copolymers (or their salts) (234, 235), polyacrylates (236), or carboxylated poly(vinyl alcohol) (237, 238). The effects of PAE resins with pectins, alginates, poly(styrenesulfonate), and carboxymethylated cornstarch have been compared with those with CMC and poly(acrylic acid) (239). Combinations of PAE resins with starch xanthates have been investigated as wet- and dry-strength additives (9, 240, 241), particularly in kraft paper (242), newsprint, and linerboard (243, 244). PAE, PAPAE, and EPA resins and various anionic polymers have also been used in various related applications such as surface strength (245), film strength (246), and synthetic pulp treatments (247-249).

Commercial Applications in Paper

The efficiencies and operating advantages of alkaline-curing resins, and the new product grades they made possible, won their immediate acceptance by the paper industry. Over three decades later, we can see aspects of both revelation and revolution in their effect.

Revelation has been effectively transmitted from ancient times to each new generation and place, by those who have assimilated that ancient truth so personally as to recreate for themselves the excitement of discovery. In the more mundane realm of technology, we can track this same process of assimilation and transmittal in the documentation on alkaline-curing resins (1, 250-256).

The spread of revelation can lead to revolution, in technology as in sociology. Revolution takes time to spread, but may spread to many neighboring areas—in technology as in sociology. Over the generation since their introduction, polymeric amine-epichlorohydrin resins have been used in a great variety of wet-strength grades. Moreover, these resins and their modifications have been used as sizing auxiliaries, production aids, and coating materials, and in nonpaper technologies as well.

Wet-strength Uses

Since their inception, alkaline-curing resins have been used in virtually every grade of paper. A few representative grades follow, in which azetidinium-type PAE resins are used for wet strength.

- Tissue and towel: facial tissue (257), consumer towel, industrial toweling and wipes, diaper liner, napkins.
- Liquid packaging board: dairy cartons, juice carton.
- Food packaging: butcher's wrap, tea bags (258), sausage casings (259), lettuce boxes, paper plates, coffee filters, bread wrap, and greaseproof wrap (260).
- Carton and corrugating: corrugating medium, linerboard, multiwall bag, bleached bag, molded products, and carrier board.
- Specialties: currency, maps, cigarette tips, waxing grades, industrial filters (261), insulating papers (262, 263), decorative laminates (264, 265), photographic paper (266), mineral fiber paper (267), sterilizable packaging (268), thermal recording paper

(269), printing (270), and filled (271) grades. Improved printing runnability and pick resistance have been claimed (271).

- Wood fiber-nonwood fiber combinations: flooring felts, synthetic fiber combinations (272, 273), synthetic fiber pretreatments (274).

PAPAE resins generally find somewhat more limited use, in both volume and variety. These tend to be used in unbleached pulps, mostly in packaging and in some grades of toweling. PAE-type epoxides are being introduced in towel, liquid packaging, and some specialty printing grades, while the APE-type epoxides are used in specialties such as nonwood pulp-cellulose combinations.

The amount of resin needed in a given grade will depend on the effectiveness of the resin, the kind of pulp, its drying conditions, and the strength requirements for that use. To generalize broadly: tissue and napkin grades frequently require 0.25–0.5% resin; food wrap and carton, 0.25–1.0%; bag papers, 0.25–0.75%; and toweling, 0.25–1.5%. (All percentages are expressed as dry weight of resin polymer solids per weight of pulp.)

A good index to the commercial importance of a resin is its approval for use in food packaging. Obtaining this clearance is a complex process which manufacturers have followed only for resins that promise substantial commercial utility. In the United States, resins allowed in food packaging include the following (76):

U.S. Food and Drug Administration Clearances*

PAE resins		Crosslinked with
Polyamide		
Adipic acid-DETA)	(one of:)
Dimethyl glutarate-DETA)	(
Isophthalic acid-DETA)	Epichlorohydrin
Itaconic acid-DETA)	Epichlorohydrin-ammonia mixture
HCHO-treated dimethyl glutarate-DETA		Epichlorohydrin-Na ₂ S ₂ O ₄ mixture
Adipic acid-DETA polyamide modified with diethylaminopropylamine, then with bis(2-chloroethyl)ether		Epichlorohydrin
Itaconic acid-caprolactam-DETA		"
PAPAE resins		**
C ₄ -C ₆ diamines and/or their self-condensation products		Epichlorohydrin
C ₄ -C ₆ diamines and/or their self-condensation products, reacted with 1,2-dichloroethane		"
Bis(hexamethylene)triamine and/or higher homologues		"
Bis(hexamethylene)triamine and/or higher homologues, reacted with 1,2-dichloroethane.		"
APE resins		
Poly(methyldiallylamine)		Epichlorohydrin

*Some of the clearances involve compositional restrictions not detailed here. This list includes only the resins allowed for wet-strength use in food packaging. It omits some compositions that are described above in the chemistry of PAE or PAPAE resins, but cleared only as retention aids or flocculants. Compositions cleared for use in the packaging of dry foods are not necessarily cleared for the packaging of aqueous or fatty foods.

***For packaging in dry foods only.*

Nonwet-strength Uses

Alkaline-curing wet-strength resins have found wide application as dispersing agents, retention aids, and promoter resins for size emulsions. Some of the specific combinations that have been investigated include:

- PAE resins with rosin size (275-278), fortified rosin size (279), styrene-maleic anhydride copolymer derivatives (280) and styrene-acrylamide-acrylic acid terpolymers (281), alkylketene dimer size (282-289), petroleum wax (282), perfluoroalkyl sizing agents (290, 291), and stearate size (292).
- Polyalkylenopolyamine-dicyandiamide-epichlorohydrin resins with alkylketene dimer or anhydride sizes (293-296) and isocyanate sizes (294).
- APE resins such as poly(diallylamine)-epichlorohydrin (PDAAE) with fortified rosin size (279) or with alkylketene dimer sizes (297, 298), poly(methyldiallylamine)-epichlorohydrin (PMDAAE) with alkylketene dimer sizes (151, 297-299), or both PDAAE and PMDAAE resins with anhydride sizes (297, 298).

PAE, PAPAE, and the APE-type resins based on poly(diallylamine) and poly(methyldiallylamine) have all been used as starch modifiers in stabilizing rosin size emulsions (300).

PAE resins made from dimeric fatty acids have been crosslinked with epichlorohydrin (301, 302) or diglycidyl-bisphenol A (303, 304) to produce paper sizes. Sizes also result from the reaction of polyalkylenopolyamines, poly(aminoamides), and amine polymers with fatty acids (305-309), fatty acid derivatives (310-314), isocyanates (315), perfluoroacids (316), or rosin (309, 317), then with epichlorohydrin.

Alkaline-curing wet-strength resins, as such or as modified versions, have been employed as retention aids for mineral fillers such as kaolin, titanium dioxide, calcium carbonate, etc. The resins have included PAE wet-strength resins of the condensation type (318-322), PAPAE-acrylate addition type (323), and PAPAE resins based on BHMT (324). PAE-type resins (32, 40, 325, 326), modified PAE resins (157, 158, 327, 328), polyamines (109, 321) and APE resins (329) have been disclosed as drainage and dewatering aids, while various PAE resins (330-333) have been used to improve dryer operation. PAE (334, 335) and PAPAE resins (336, 337, 324) have been evaluated as flocculants in mill effluents and savealls.

Alkaline-curing resins and their modifications improve such paper properties as dimensional stability (338, 339), dry strength (340), porosity (341), and coating quality (342, 343). PAE resins have served as insolubilizing agents for such materials as starch and water-soluble cellulosic polymers (344), latexes (345), and inks (346). PAPAE resins (347) and their polyamine-dicyandiamide-epichlorohydrin-formaldehyde versions (348) have been used as auxiliaries in dyeing, and (in conjunction with carboxylated polymers) in the decoration of textiles (349). Combinations of polyamine-epichlorohydrin resins and anionic polymers have been used as encapsulants for dyes in carbonless copy papers (350).

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